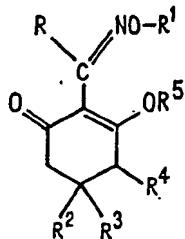


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(54) Herbicidal substituted 2-[1-(oxyamino)-alkylidene]-cyclohexane-1,3-diones and derivatives

(57) Herbicidally active compounds, particularly against grassy weeds, are represented by the general formula:



wherein R is alkyl or 1 to 6 carbon atoms or phenyl; R¹ is haloalkyl or 1 to 6 carbon atoms, haloalkenyl of 2 to 6 carbon atoms, haloaryl of 6 to 10 carbon atoms, halobenzyl, all of which contain 1 to 3 halogen atoms,

cycloalkyl of 5 to 7 carbon atoms, or benzyl substituted by 1 to 3 alkyl groups of 1 to 4 carbon atoms or haloalkyl groups of 1 to 4 carbon atoms and 1 to 9 halogen atoms; R² and R³ are independently hydrogen, alkyl of 1 to 3 carbon atoms, alkylthio of 1 to 6 carbon atoms, or alkylthioalkyl of 2 to 8 carbon atoms; R⁴ is hydrogen or carbalkoxy of 2 to 4 carbon atoms; and R⁵ is hydrogen, a cation, or



wherein R⁶ is alkyl of 1 to 6 carbon atoms or aryl of 6 to 10 carbon atoms.

Preferably R, R² and R³ are alkyl and R⁴ and R⁵ are hydrogen.

The compounds may be used in both pre- and post-emergent applications.

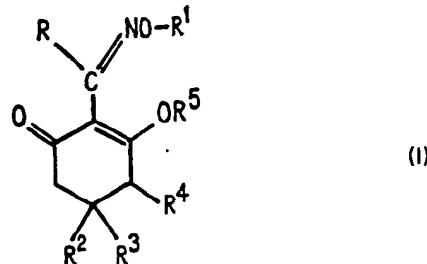
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SPECIFICATION

Herbicidal substituted 2-[1-(oxyamino)-alkylidene]-cyclohexane-1,3-diones

This invention relates to novel herbicidal compounds, compositions and method of use thereof. It has been found that novel haloalkyl, haloalkenyl and haloaryl-substituted 2-[1-(oxyamino)-alkylidene]-cyclohexane-1,3-diones are particularly useful as grassy herbicides in both pre- and post-emergent applications.

The compounds of the invention have the structural formula (I):



wherein R is alkyl of 1 to 6 carbon atoms or phenyl; R¹ is haloalkyl of 1 to 6 carbon atoms, haloalkenyl of 2 to 6 carbon atoms, haloaryl of 6 to 10 carbon atoms, halobenzyl, all of which contain 1 to 3 halogen atoms; cycloalkyl of 5 to 7 carbon atoms, or benzyl substituted by 1 to 3 alkyl groups of 1 to 4 carbon atoms or haloalkyl groups of 1 to 4 carbon atoms and 1 to 9 halogen atoms; R² and R³ are independently hydrogen, alkyl of 1 to 3 carbon atoms, alkylthio of 1 to 6 carbon atoms, or alkylthioalkyl of 2 to 8 carbon atoms; R⁴ is hydrogen, or carbalkoxy of 2 to 4 carbon atoms; and R⁵ is hydrogen, a cation, or



wherein R⁶ is alkyl of 1 to 6 carbon atoms or aryl of 6 to 10 carbon atoms.

A preferred class of compounds within the class defined by formula I is that wherein R⁴ and R⁵ are hydrogen, whilst a particularly preferred class is that wherein R⁴ and R⁵ are hydrogen and R, R² and R³ are alkyl, i.e. the substituted 2-[1-(oxyamino)-alkylidene]-5,5-dialkylcyclohexane-1,3-diones.

Representative R groups are methyl, ethyl, n-propyl, isopropyl, n-butyl, isopentyl, neopentyl, n-hexyl and phenyl.

Preferably R is alkyl of 1 to 6 carbon atoms. Most preferably R is alkyl of 1 to 3 carbon atoms. Most preferably R is ethyl or propyl.

Representative R¹ groups are chloromethyl, bromomethyl, fluoromethyl, 2-chloroethyl, 2-bromoethyl, 3,4-dichlorobutyl, 6-chlorohexyl, 3-cis-chloroallyl, 2,3-cis-dichloroallyl, 2-chloroallyl, 4,4-dichloro-but-3-enyl, 4-bromo-3-bromomethyl-but-2-enyl, 5,5-dibromo-4-methyl-pent-2-enyl, 2,5-dichloro-hex-3-enyl, p-fluorophenyl, p-fluorobenzyl, p-chlorobenzyl, p-bromophenyl, p-bromobenzyl, 3,4-dichlorophenyl, 3,4-dichlorobenzyl, 2-fluorophenyl, 2-fluorobenzyl, 2,4,6-trichlorophenyl, 2,4,6-trichlorobenzyl, 1-bromo-naphth-2-yl, 2-chloronaphth-1-yl, cyclopentyl, cyclohexyl, cycloheptyl, p-methylbenzyl, m-methylbenzyl, 2,4,6-triethylbenzyl, p-butylbenzyl, p-isopropylbenzyl, and p-trifluoromethylbenzyl.

Preferably R¹ is haloalkenyl of 2 to 6 carbon atoms and 1 to 3 halogen atoms or halobenzyl of 1 to 3 halogen atoms. Most preferably R¹ is haloallyl, particularly, 3-cis-chloroallyl.

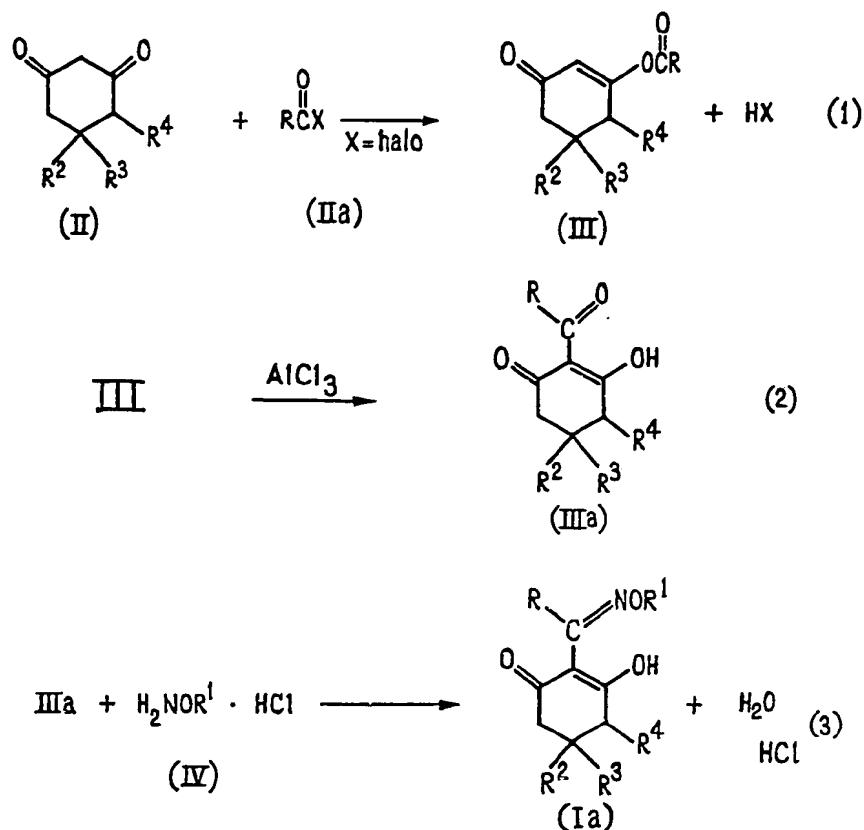
Representative R² and R³ groups are hydrogen, methyl, ethyl, propyl, methylthio, ethylthio, n-butylthio, methylthiomethyl, ethylthiomethyl, propylthiopropyl, ethylthiohexyl.

Preferably R² and R³ are alkyl of 1 to 3 carbon atoms. Most preferably R² and R³ are both methyl.

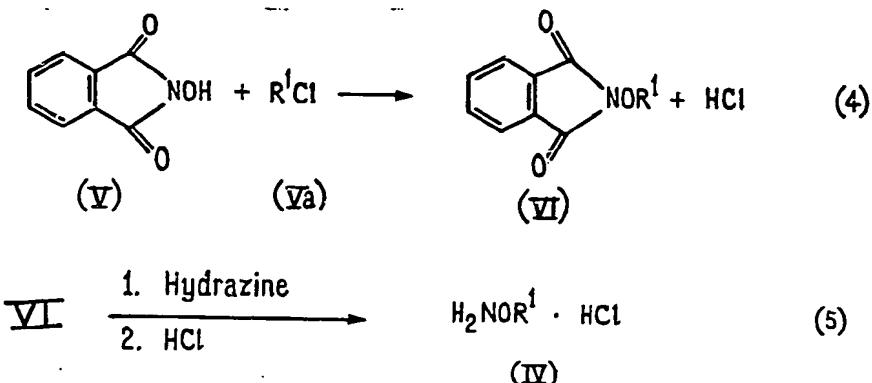
Representative R⁴ groups are hydrogen, carbomethoxy, carboethoxy, carbopropoxy. Preferably R⁴ is hydrogen.

Representative R⁵ groups are hydrogen, NH₄⁺, Na⁺, K⁺, Ca⁺⁺, acetyl, propionyl, butyryl, isobutyryl, isovaleryl, 3,3-dimethylbutyryl, benzoyl, 1-naphthoyl, 2-naphthoyl. Preferably R⁵ is hydrogen.

The compounds of the invention may be prepared according to the following scheme:



The appropriate intermediates of the formula (IV) may be made according to the following reaction sequence:



Compounds of the formula (I) wherein R⁵ is other than hydrogen may be prepared according to conventional procedures by treating the hydroxy compound (Ia) with an appropriate basic salt to yield 10 compounds wherein R⁵ is Na⁺, NH₄⁺, Ca⁺⁺, etc. Similarly, the hydroxy compound (Ia) may be acylated by treatment with an appropriate acid halide to yield compounds wherein R⁵ is 10



Reaction (1) above may be performed at ambient temperature employing substantially equimolar amounts of the dione (II) and acid halide (IIa). Preferably the acid chloride (X=Cl) is used. The reaction 15 may be conducted in an organic solvent, such as, halogenated hydrocarbons, ethers or glycols. It is preferred that a base be present, such as an organic amine or alkali metal carbonate salt, in order to quench the hydrogen halide which is evolved. Preferred organic amines are pyridine and trialkylamines such as triethylamine. Pressure conditions are critical and atmospheric pressure may be conveniently employed.

- Reaction (2) may be performed in an inert organic solvent, such as, halogenated hydrocarbons or ethers. At least two moles of aluminum chloride per mole of ester (III) is used. Upon work-up, the crude product must be quenched with a proton-donor, preferably a mineral acid such as hydrochloric acid, to produce the trione (IIIa). 5
- 5 Reaction (3) is a conventional oxime forming condensation. Since the hydrochloride salt (IV) is employed, it is first neutralized with a base, preferably an alkali metal alkoxide, before combining with the trione (IIIa). The reaction may be performed in an inert organic solvent, preferably lower alcohols. 5
- Reaction (4) is a conventional alkylation and may be performed in inert organic solvents such as dimethylsulfoxide, acetonitrile, ethers, glycol ethers or hydrocarbons. The reaction is performed in presence of a base, such as potassium carbonate at ambient temperature. 10
- 10 Reaction (5) may be performed at elevated temperatures, preferably 30—100°C. The phthalimide (VI) is preferably heated at atmospheric pressure with slight molar excess of hydrazine in an inert organic solvent, such as a lower alcohol, to reflux temperature. The crude mixture is then cooled and quenched with a mineral acid, preferably hydrochloric acid, yielding the product salt (IV). 10
- 15 As an alternative to reactions (1) and (2) above the trione (IIIa) may be formed in one step by treating the dione (II) with the acid halide (IIIa) in a halogenated hydrocarbon solvent, preferably carbon tetrachloride, in the presence of trifluoromethyl sulfonic acid. The reaction is performed at elevated temperature (30—150°C) and is complete within 90 hours but yields a mixture of products. Since the combined reaction time of reactions (1) and (2) is about 24 hours, and results in a purer product, the 15
- 20 two-step sequence of reactions (1) and (2) is preferred to the one-step alternative. The respective products of the above reactions may be isolated and purified by conventional techniques such as chromatography, distillation, crystallization, etc., when appropriate. The products in the following Examples and Table A were identified by infrared and nmr spectroscopy and elemental analysis. 20
- EXAMPLE 1** 25
- 25 Preparation of 2-[1-(3'-chloroallyloxyamino)-butylidene]-5,5-dimethylcyclohexane-1,3-dione
- A. Dimedone (5,5-dimethylcyclohexane-1,3-dione, 99%, 14.2 g), pyridine (9 ml) and methylene chloride (100 ml) were mixed in a flask and butyryl chloride (11.4 g) was added dropwise. The mixture was stirred for 26 hours at room temperature and filtered. The filtrate was washed with HCl (6N, 100 ml), water (100 ml), saturated Na_2CO_3 (50 ml), water (50 ml), dried (MgSO_4). The solvent was removed under reduced pressure to yield 3-butyroxy-5,5-dimethylcyclohex-2-ene-1-one as a yellow liquid. 30
- B. To a dry flask containing methylene chloride (30 ml) and aluminum chloride (26.67 g) at ice bath temperature was added dropwise a solution of the product of step A (21.03 g) in dichloromethane (50 ml). The mixture was stirred for 2-1/2 hours then poured into 100 ml cold 6N HCl slowly with stirring. The mixture stood overnight. The organic phase was collected and washed with saturated Na_2CO_3 (100 ml) and water (100 ml). The solvent was stripped to yield 15.9 g yellow liquid. The Na_2CO_3 wash was acidified to pH 2 with concentrated HCl, extracted with CH_2Cl_2 and stripped to yield 4.8 g yellow liquid, identical to the composition of the 15.9 g of product. The combined products yielded 20.7 g 2-butyro-5,5-dimethylcyclohexane-1,3-dione. 35
- C. To a solution of N-hydroxypythalimide (33.6 g) in dimethylsulfoxide (200 ml) was added anhydrous potassium carbonate (28 g). After 10 minutes, 2,3-dichloropropene (20 ml) was added and the mixture was stirred at room temperature overnight. The mixture was poured into 1.2 liter ice-water and the resultant white precipitate was collected, washed with cold water (2 x 100 ml), air-dried and crystallized from 1.1 liter ethyl alcohol. Yield: 41.0 g. N-(3-chloroallyloxy)-phthalimide, white needles. 40
- D. The product from step C (21.2 g), absolute ethanol (650 ml) and hydrazine (3.7 g) were stirred in a flask and gradually heated to reflux. After 2 hours the mixture was cooled to room temperature, added to concentrated HCl (12.5 ml), then cooled to 0°. The precipitate was collected and washed with cold ethanol and water. The washings were concentrated to yield 21.5 g of the crude product. This product was slurried with 50 ml methanol and the white solid was filtered and dried to yield 3.3 g of the crystalline product. The combined washings and filtrates were concentrated, and recrystallized (50 ml acetonitrile, 50 ml ether) to yield an additional 5.5 g of white crystalline product, 3-chloroallyloxyamine hydrochloride. 45
- E. To a solution of sodium methoxide (460 mg) in methanol (10 ml) was added the product of step D (1.22 g) and the suspension was stirred at room temperature for 15 minutes. To this suspension was added a solution of 2-butyro-5,5-dimethylcyclohexane-1,3-dione (see step B above) in 10 ml methanol. After stirring for two days at room temperature, the solution was concentrated in vacuo. The residue was taken up in 30 ml ethyl acetate and 2.5 ml 10% NaOH, whereupon three layers formed. The bottom two layers were collected, cooled, acidified with con. HCl (pH 1) and extracted twice with 30 ml methylene chloride. The methylene chloride extracts were combined, washed with water (2 x 20 ml), dried (MgSO_4) and concentrated in vacuo to yield the liquid product, 2-[1-(3'-chloroallyloxyamino)-butylidene]-5,5-dimethylcyclohexane-1,3-dione. See compound No. 3 in Table A. 50
- 55
- 55 Preparation of 2-[1-(3'-chloroallyloxyamino)-propylidene]-5,5-dimethylcyclohexane-1,3-dione
- A. According to the procedure of Example 1A, 5,5-dimethylcyclohexane-1,3-dione (14.2 g) and
- 60

EXAMPLE 2

Preparation of 2-[1-(3'-chloroallyloxyamino)-propylidene]-5,5-dimethylcyclohexane-1,3-dione

A. According to the procedure of Example 1A, 5,5-dimethylcyclohexane-1,3-dione (14.2 g) and

propionyl chloride (9.7 g) were reacted in pyridine (9 ml) and methylene chloride (100 ml) to yield 21.0 g. 3-propionoxy-5,5-dimethylcyclohex-2-en-1-one.

B. The product of Example 2A (19.62 g) and aluminum chloride (26.67 g) were treated according to the procedure of Example 1B to yield 17.9 g. 2-propiono-5,5-dimethyl-cyclohexane-1,3-dione.

C. The product made according to Example 1D (1.22 g) and the product from Example 2B (1.65 g) were treated according to the procedure of Example 1E to yield the liquid product 2-[1-(3'-chlorallyloxyamino)-propylidene]-5,5-dimethylcyclohexane-1,3-dione. See Compound No. 4 in Table A. 5

UTILITY

The compounds of the present invention are, in general, herbicidal in both pre- and post-emergent applications. For pre-emergent control of undesirable vegetation, the herbicidal compounds will be applied in herbicidally effective amounts to the locus or growth medium of the vegetation, e.g., soil infested with seeds and/or seedlings of such vegetation. Such application will inhibit the growth of or kill the seeds, germinating seeds and seedlings. For post emergent applications, the herbicidal compounds will be applied directly to the foliage and other plant parts. Generally, the herbicidal compounds of the invention are particularly effective against grassy weeds. Some may be selective with respect to the type of application and/or type of weed. 10
15

The compounds, when applied to growing plants above the ground in such an amount that the compounds will not kill beneficial plants, also show efficient plant growth regulating or retarding effects and may be advantageously employed, for example, to prevent or retard the growth of lateral buds in plants and to promote the thinning out of superfluous fruits in various fruit trees. 20

The compounds can be applied in any of a variety of compositions. In general, the compounds can be extended with a biologically inert carrier material of the kind used and commonly referred to in the art, such as inert solids, water and organic liquids.

The compounds will be included in such compositions in sufficient amount so that they can exert an herbicidal or growth-regulating effect. Usually from about 0.5 to 95% by weight of the compounds are included in such formulations. 25

Solid compositions can be made with inert powders. The compositions thus can be homogeneous powders that can be used as such, diluted with inert solids to form dusts, or suspended in a suitable liquid medium for spray application. The powders usually comprise the active ingredient admixed with minor amounts of conditioning agent. Natural clays, either absorptive, such as attapulgite, or relatively non-absorptive, such as china clays, diatomaceous earth, synthetic fine silica, calcium silicate and other inert solid carriers of the kind conventionally employed in powdered herbicidal compositions can be used. The active ingredient usually makes up from 0.5—90% of these powder compositions. The solids ordinarily should be very finely divided. For conversion of the powders to dusts, talc, pyrophyllite, and the like, are customarily used. 30
35

Liquid compositions including the active compounds described above can be prepared by admixing the compound with a suitable liquid diluent medium. Typical of the liquid media commonly employed are methanol, benzene, toluene, and the like. The active ingredient usually makes up about 0.5 to 50% of these liquid compositions. Some of these compositions are designated to be used as such, and others to be extended with large quantities of water. 40

Compositions in the form of wettable powders or liquids can also include one or more surface-active agent, such as wetting, dispersing or emulsifying agents. The surface-active agents cause the compositions of wettable powders or liquids to disperse or emulsify easily in water to give aqueous sprays. 45

The surface-active agents employed can be of the anionic, cationic or nonionic type. They include, for example, sodium long-chain carboxylates, alkyl aryl sulfonates, sodium lauryl sulfate, polyethylene oxides, lignin sulfonates and other surface-active agents.

When used as a pre-emergent treatment, it is desirable to include a fertilizer, an insecticide, a fungicide or another herbicide. 50

The amount of active compound or composition administered will vary with the particular plant part or plant growth medium which is to be contacted, the general location of application — i.e., sheltered areas such as greenhouses, as compared to exposed areas such as fields — as well as the desired type of control. Generally for both pre- and post-emergent herbicidal control, the compounds of the invention are applied at rates of 0.2 to 60 kg/ha, and the preferred rate is in the range 0.5 to 40 kg/ha. For plant growth regulating or retarding activity, it is essential to apply the compounds at a concentration not so high as to kill the plants. Therefore, the application rates for plant growth regulating or retarding activity will generally be lower than the rate used for killing the plants. Generally, such rates vary from 0.1 to 5 kg/ha, and preferably from 0.1 to 3 kg/ha. 55

Herbicidal tests on representative compounds of the invention were made using the following methods. 60

Pre-Emergent Herbicidal Test

An acetone solution of the test compound was prepared by mixing 500 mg of the compound, 158

mg of a nonionic surfactant and 20 ml of acetone. Twenty ml of this solution was added to 80 ml of water to give the test solution.

5 Seeds of the test vegetation were planted in a p t of soil and the test solution was sprayed uniformly onto the soil surface at a dose of 27.5 micrograms/cm². The pot was watered and placed in a 5 greenhouse. The pot was watered intermittently and observed for seedling emergence, health of emerging seedlings, etc., for a 3-week period. At the end of this period, the herbicidal effectiveness of the compound was rated based on the physiological observations. A 0-to-100 scale was used, 0 representing no phytotoxicity, 100 representing complete kill. The results of these tests appear in Table I.

10 In follow-up tests, the procedure above was repeated using diluted test solution which was sprayed onto the soil surface at various dosages. The results of these tests appear in Table II. 10

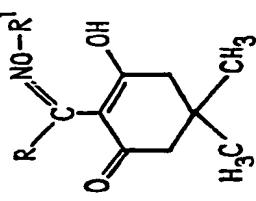
Post-Emergent Herbicidal Test

15 The test compound was formulated in the same manner as described above for the pre-emergent test. This formulation was uniformly sprayed on 2 similar pots of 24-day-old plants (approximately 15 to 15 25 plants per pot) at a dose of 27.5 micrograms/cm². After the plants had dried, they were placed in a greenhouse and then watered intermittently at their bases, as needed. The plants were observed periodically for phytotoxic effects and physiological and morphological responses to the treatment. After 3 weeks, the herbicidal effectiveness of the compound was rated based on these observations. A 0-to-20 20 100 scale was used, 0 representing no phytotoxicity and 100 representing complete kill. The results of these tests appear in Table I.

In follow-up tests, the procedure above was repeated using diluted test solution which was sprayed onto the soil surface at various dosages. The results of these tests appear in Table II.

TABLE A

Compounds of the Formula



ANALYSIS

No.	R	R'	mp °C	C				H				N			
				Calc.	Fd.	Calc.	Fd.	Calc.	Fd.	Calc.	Fd.	Calc.	Fd.	Calc.	Fd.
1	C ₂ H ₅	CH ₂ CCl=CH ₂	Oil	58.84	59.33	7.05	7.43	4.90	4.90	5.06	5.06				
2	CH ₃ CH ₂ CH ₂	CH ₂ CCl=CH ₂	Oil	60.09	59.41	7.40	7.61	4.67	4.67	4.70	4.70				
3	CH ₃ CH ₂ CH ₂	Cis-CH ₂ CH=CHCl	Oil	60.09	62.13	7.40	7.80	4.67	4.67	4.88	4.88				
4	C ₂ H ₅	Cis-CH ₂ CH=CHCl	Oil	58.84	58.69	7.05	7.22	4.90	4.90	5.06	5.06				
5	CH ₃ CH ₂ CH ₂	CH ₂ -C(Cl)C ₆ H ₄ -CH ₂	Oil	65.23	66.29	6.91	7.36	4.00	4.00	4.05	4.05				
6	C ₂ H ₅	CH ₂ -C(Cl)C ₆ H ₄ -CH ₂	Oil	64.37	64.56	6.6	6.81	4.17	4.17	4.17	4.17				
7	CH ₃ CH ₂ CH ₂	CH ₂ -C(Cl)C ₆ H ₄ -CH ₂	Oil	65.23	65.16	6.91	7.18	4.00	4.00	3.61	3.61				

TABLE A (Continued)

No.	R	R'	mp °C	ANALYSIS					
				C		H		N	
				Calc.	Fd.	Calc.	Fd.	Calc.	Fd.
8	C ₂ H ₅	CH ₂ -C ₆ H ₄ -Cl	Oil	64.37	63.93	6.60	6.74	4.17	3.81
9	CH ₃ CH ₂ CH ₂	CH ₂ -C ₆ H ₄ -F	Oil	68.45	68.83	7.26	7.92	4.20	4.25
10	C ₂ H ₅	CH ₂ -C ₆ H ₄ -F	Oil	67.69	68.19	6.98	7.70	4.39	4.60
11	CH ₃ CH ₂ CH ₂	CH ₂ -C ₆ H ₄ -F	Oil	68.45	71.78	7.26	7.88	4.20	4.67
12	C ₂ H ₅	CH ₂ -C ₆ H ₄ -F	Oil	67.69	67.88	6.98	7.26	4.39	4.41
13	CH ₃ CH ₂ CH ₂	CH ₂ -C ₆ H ₄ -Cl	Oil	65.23	66.84	6.91	7.4	4.00	4.34

TABLE A (Continued)

ANALYSIS

No.	R	R'	mp °C	C			H			N		
				Calc.	Fd.	Calc.	Fd.	Calc.	Fd.	Calc.	Fd.	Calc.
14	C ₂ H ₅		Oil	64.37	65.45	6.60	6.99	4.17	4.33			
15	CH ₃ CH ₂ CH ₂		70-71	59.38	60.34	6.03	6.36	3.65	3.83			
16	CH ₃ CH ₂ CH ₂	(trans)-CH ₂ CH=CHCl	Oil	60.09	62.05	7.40	8.31	4.67	4.9			
17	CH ₃		Oil	61.33	61.45	5.49	6.43	4.43	4.56			
18	CH ₃		84.7	54.89	55.55	4.61	5.07	4.27	4.17			
19	CH ₃ (CH ₂) ₃	CH ₂ CCl=CH ₂	Oil	61.23	61.25	7.71	8.36	4.46	4.16			
20	CH ₃	CH ₂ CCl=CH ₂	Oil	57.76	57.11	6.68	6.96	5.15	4.98			
21	CH ₃ CH ₂ CH ₂	CH ₂ CCl=CHCl	Oil	53.90	54.52	6.33	6.8	4.19	4.20			
22	CH ₃	CH ₂ CCl=CHCl	Oil	50.99	50.77	5.60	6.02	4.57	4.6			

TABLE A (Continued)

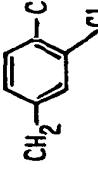
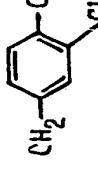
No.	R	R'	mp °C	ANALYSIS					
				C		H		N	
				Calc.	Fd.	Calc.	Fd.	Calc.	Fd.
23	CH ₃ (CH ₂) ₃	CH ₂ CCl = CHCl	Oil	55.18	54.16	6.66	7.06	4.02	3.99
24	C ₂ H ₅	CH ₂ CCl = CHCl	Oil	52.51	52.58	5.98	4.97	4.37	4.37
25	CH ₃ (CH ₂) ₃	CH ₂ - 	Oil	69.15	69.23	7.54	7.93	4.03	4.15
26	(CH ₃) ₂ CHCH ₂	CH ₂ - 	Oil	69.15	69.43	7.54	7.89	4.03	4.04
27	CH ₃	(trans)-CH ₂ CH = CHCl	Oil	57.46	62.13	6.68	7.48	5.15	5.56
28	C ₂ H ₅	(trans)-CH ₂ CH = CHCl	Oil	58.84	56.29	7.05	6.93	4.90	4.71
29	(CH ₃) ₂ CHCH ₂	(trans)-CH ₂ CH = CHCl	Oil	61.23	59.71	7.71	7.95	4.46	4.11
30	C ₂ H ₅	CH ₂ - 	Oil	58.39	55.23	5.72	5.93	3.78	3.35
31	CH ₃ CH ₂ CH ₂	CH ₂ - 	Oil	59.40	56.53	6.03	6.23	3.64	3.22

TABLE A (Continued)

No.	R	R ¹	mp °C	ANALYSIS					
				C		H		N	
Calc.	Fd.	Calc.	Fd.	Calc.	Fd.	Calc.	Fd.	Calc.	Fd.
ANALYSIS									
32	CH ₃ (CH ₂) ₃	CH ₂ -Cl-C ₆ H ₄ -Cl	Oil	60.30	58.37	6.33	6.37	3.52	3.24
33	(CH ₃) ₂ CHCH ₃	CH ₂ -Cl-C ₆ H ₄ -Cl	Oil	60.30	57.62	6.33	6.37	3.52	3.12
34	CH ₃ CH ₂ CH ₃	CH ₂ CCl=CH ₂	Oil	57.06	54.85	6.76	6.83	3.91	4.66
35	CH ₃ CH ₂ CH ₃	CH ₂ CH=CClCH ₃	Oil	61.23	62.67	7.71	7.90	4.46	5.12
36	CH ₃	CH ₂ -Cl-C ₆ H ₄	Oil	63.45	61.30	6.26	6.14	4.35	3.98
37	CH ₃	(cis)-CH ₂ CH=CHCl	Oil	57.46	59.93	6.78	7.01	5.02	5.57
38	CH ₃	CH ₂ CH=CClCH ₃	Oil	58.84	57.69	7.05	7.55	4.90	5.57
39	CH ₃	CH ₂ -F-C ₆ H ₄	41-42	66.87	67.56	6.60	6.85	4.59	4.61
40	CH ₃ (CH ₂) ₃	CH ₂ CH ₂ Cl	Oil	59.69	61.65	8.02	8.46	4.64	4.04
41	CH ₃ CH ₂ CH ₃	(trans)-CH ₂ CH=CHCl	Oil	57.06	57.38	6.76	7.05	3.91	4.76

TABLE A (Continued)
ANALYSIS

No.	R	R ¹	mp °C	C				H				N			
				Calc.	Fd.	Calc.	Fd.	Calc.	Fd.	Calc.	Fd.	Calc.	Fd.	Calc.	Fd.
42	C ₂ H ₅		70-71	58.39	58.71	57.72	58.89	3.78	3.97						
43	CH ₃ CH ₂ CH ₂	(trans)-CH ₂ CH=CHCH ₂ Cl	Oil	61.24	62.1	7.70	8.01	4.46	4.08						
44	CH ₃	CH ₃ CH ₂ Cl	Oil	55.49	55.88	6.98	7.02	5.39	4.18						
45	C ₂ H ₅	CH ₂ CH=CClCH ₃	Oil	60.10	59.96	7.40	7.57	4.67	4.67						
46	C ₂ H ₅	(cis)-CH ₂ CH=CHCH ₂ Cl	Oil	60.10	60.21	7.40	7.71	4.67	3.74						
47	C ₂ H ₅		54-60	66.47	67.43	6.69	7.26	3.88	4.08						
48	C ₂ H ₅		Oil	61.78	62.55	6.00	6.17	3.79	3.93						
49	CH ₃ CH ₂ CH ₂		Oil	62.35	63.3	6.31	6.63	3.65	3.76						

TABLE A (Continued)

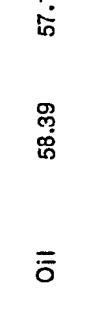
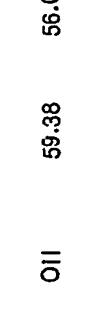
No.	R	R ¹	mp °C	C		H		N	
				Calc.	Fd.	Calc.	Fd.	Calc.	Fd.
50	C ₂ H ₅		Oil	58.39	57.10	5.72	5.50	3.78	3.84
51	CH ₃ CH ₂ CH ₂		Oil	59.38	56.02	6.03	5.58	3.64	3.78
A	CH ₃ CH ₂ CH ₂	CH ₂ CH-CH ₂	(See Patent No. 4,011,256)						
52	CH ₃ CH ₃		Oil	61.78	60.9	6.00	6.5	3.79	3.87
53	CH ₃ CH ₂ CH ₃		Oil	62.65	61.63	6.31	7.00	3.65	4.16

TABLE I — HERBICIDAL ACTIVITY

Pre/Post % Control (27.5 gamma/cm²)

No.	L	M	P	C	W	O
1	0/0	0/0	0/0	100/75	100/100	50/93
2	0/50	20/50	30/35	100/60	100/98	90/68
3	30/25	10/20	35/20	100/100	100/100	100/100
4	40/10	23/25	35/0	100/100	100/100	100/100
5	0/35	40/55	45/45	98/50	100/68	55/15
6	40/40	60/58	43/63	65/25	80/40	30/0
7	0/45	0/55	0/28	100/70	100/100	100/100
8	0/25	0/65	0/40	100/75	100/100	85/100
9	0/55	0/65	0/50	100/20	100/88	55/30
10	0/45	0/45	0/30	98/35	100/83	48/23
11	20/40	0/35	0/23	100/53	100/100	100/100
12	15/23	0/30	0/13	100/60	100/100	68/100
13	0/23	0/73	0/0	98/35	98/80	75/88
14	0/13	0/60	0/0	95/33	100/88	65/78
15	0/0	0/0	0/0	95/40	100/95	65/53
16	0/40	0/60	0/20	100/90	100/100	73/100
17	0/45	0/30	0/0	0/0	0/0	0/0
18	0/25	10/35	10/23	0/0	0/0	0/0
19	0/55	0/68	0/30	45/23	93/35	35/10
20	30/0	0/0	0/0	65/70	98/100	35/20
21	0/55	0/88	0/28	100/45	100/98	60/88
22	20/23	0/60	0/23	55/25	100/98	35/0
23	0/38	0/98	0/28	55/10	100/70	30/10
24	30/35	0/75	0/23	100/28	100/95	55/38
25	25/40	0/88	0/30	45/20	33/0	33/0
26	0/30	0/55	0/0	85/20	95/80	53/100
27	0/0	0/0	0/0	98/65	100/100	40/80
28	20/28	10/—	0/0	100/60	100/100	53/100
29	0/28	0/70	0/0	70/0	100/98	50/45
30	0/50	0/40	0/48	63/23	100/80	35/20

TABLE I (Cont'd)

No.	L	M	P	C	W	O
31	0/28	0/38	0/0	45/20	100/45	55/55
32	0/35	0/60	0/0	0/0	0/25	0/0
33	0/43	0/23	0/40	0/0	25/15	15/0
34	0/25	0/0	0/0	80/30	100/100	53/98
35	48/33	0/63	0/0	95/23	100/93	43/75
36	35/20	0/0	25/0	98/55	100/100	48/90
37	50/35	0/55	0/0	100/90	100/100	53/98
38	0/15	0/0	0/0	98/60	100/98	35/20
39	35/33	0/0	0/0	100/68	100/100	43/93
40	70/25	0/38	0/25	40/10	50/43	30/0
41	33/13	0/0	13/15	100/55	100/100	65/98
42	18/28	0/0	15/33	53/0	53/28	0/25
43	0/25	0/0	0/0	25/25	55/60	20/20
44	60/0	0/0	0/0	55/60	100/93	35/35
45	0/30	0/0	0/0	63/35	100/95	45/75
46	15/23	0/0	0/0	15/25	60/45	15/20
47	0/0	0/0	0/0	100/70	100/100	35/100
48	43/15	20/55	15/15	60/30	60/58	45/15
49	35/15	0/0	0/15	100/50	90/65	55/90
50	0/25	0/45	0/23	40/20	85/40	0/0
51	0/35	0/80	0/40	70/20	98/58	30/20
52	60/0	70/55	35/40	—/90	100/95	78/88
53	0/25	0/55	0/45	—/80	100/100	100/100

L = Lambsquarter (*Chenopodium album*)M = Mustard (*Brassica arvensis*)P = Pigweed (*Amaranthus retroflexus*)C = Crabgrass (*Digitaria sanguinalis*)W = Watergrass (*Echinochloa crusgalli*)O = Wild Oats (*Avenua fatua*)

TABLE II — HERBICIDAL ACTIVITY

Pre/Post % Control (rate in gamma/cm²)

No.	Rate	Soybeans	Rice	L	M	P	C	W	O
1	11	0/0	99/82	37/0	0/25	0/3	97/52	100/100	80/65
	4.4	0/0	73/3	0/0	0/0	0/0	93/7	100/99	80/7
	1.8	0/0	27/0	0/0	0/0	0/0	52/0	99/95	28/0
	0.7	0/0	5/0	0/0	0/0	0/0	23/0	55/7	0/0
2	27.5	—/25	—/55	—/50	—/55	—/35	—/60	—/98	—/68
	4.4	0/—	95/—	0/—	0/—	0/—	23/—	55/—	0/—
	1.8	0/—	83/—	0/—	0/—	0/—	88/—	100/—	77/—
	0.7	0/—	60/—	0/—	0/—	0/—	83/—	100/—	58/—
3	4.4	0/10	100/95	0/0	0/0	0/0	93/75	100/100	95/99
	1.8	0/0	92/88	0/0	0/0	0/0	82/27	100/100	90/93
	0.7	0/0	73/60	0/0	0/0	0/0	53/20	100/97	62/52
	0.28	0/0	27/7	0/0	0/0	0/0	22/0	100/95	33/23
4	4.4	0/0	100/100	0/0	0/0	0/0	98/100	100/100	95/99
	1.8	0/0	100/98	0/0	0/0	0/0	98/100	100/100	87/95
	0.7	0/0	97/95	0/0	0/0	0/0	82/83	100/95	58/—
	0.28	0/0	80/50	0/0	0/0	0/0	67/12	100/90	0/0
5	27.5	—/10	—/10	—/35	—/55	—/45	—/50	—/68	—/15
	4.4	0/—	12/—	0/—	0/—	0/—	25/—	78/—	20/—
	1.8	0/—	0/—	0/—	0/—	0/—	7/—	58/—	0/—
	0.7	0/—	0/—	0/—	0/—	0/—	0/—	0/—	0/—
	0.28	0/—	0/—	0/—	0/—	0/—	0/—	0/—	0/—
6	27.5	20/20	48/13	40/40	60/58	43/63	65/25	80/40	30/0
7	4.4	0/1	100/96	0/0	0/0	0/0	77/0	100/100	90/100
	1.8	0/3	92/60	0/0	0/0	0/0	57/0	100/98	78/97
	0.7	0/0	90/0	0/0	0/0	0/0	8/0	85/92	67/85
	0.28	0/0	30/0	0/0	0/0	0/0	0/0	25/40	15/7

TABLE II (Cont'd)

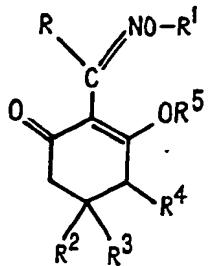
No.	Rate	Soybeans	Rice	L	M	P	C	W	O
8	4.4	0/4	100/96	20/0	0/0	0/0	87/7	100/98	95/76
	1.8	0/0	83/57	0/0	0/0	0/0	13/0	87/95	7/32
	0.7	0/0	18/12	0/0	0/0	0/0	0/0	22/73	0/0
	0.28	0/0	0/0	0/0	0/0	0/0	0/0	7/0	0/0
11	4.4	2/0	97/72	0/0	0/0	0/0	57/0	100/100	48/100
	1.8	0/0	40/30	0/0	0/0	0/0	0/0	63/95	15/68
	0.7	0/0	0/0	0/0	0/0	0/0	0/0	20/73	0/7
	0.28	0/—	0/—	0/0	0/0	0/0	0/—	0/—	0/—
16	4.4	0/0	78/57	0/0	0/0	63/0	60/25	100/100	27/92
	1.8	0/0	65/10	0/0	0/0	65/0	0/3	92/98	0/15
	0.7	0/0	3/3	0/0	0/0	0/0	0/0	40/95	0/0
	0.28	0/0	0/0	0/0	0/0	0/0	0/0	0/32	0/0
19	27.5	0/10	13/0	0/55	0/68	0/30	45/23	93/58	35/10
20	27.5	0/0	50/60	0/30	0/0	0/0	70/65	100/98	20/35
22	27.5	0/0	43/55	20/23	0/60	0/23	55/25	100/98	35/0
23	27.5	0/20	20/10	0/38	0/98	0/28	55/10	100/70	30/10
24	27.5	0/0	78/50	30/35	0/75	0/23	100/28	100/95	78/38
27	4.4	0/0	77/87	0/0	0/0	0/0	—/93	100/100	13/17
	1.8	0/0	53/10	0/0	0/0	0/0	—23	43/93	0/0
	0.7	0/0	0/0	0/0	0/0	0/0	—/0	0/13	0/0
28	27.5	—/0	—/?	—/—	—/—	—/0	—/—	—/—	—/—
	4.4	0/—	72/—	0/—	0/—	0/—	—/—	100/—	47/—
	1.8	0/—	53/—	0/—	0/—	0/—	—/—	92/—	0/—
	0.7	0/—	10/—	0/—	0/—	0/—	—/—	63/—	0/—
	0.28	0/—	0/—	0/—	0/—	0/—	—/—	0/—	0/—

TABLE II (Cont'd)

No.	Rate	Soybeans	Rice	L	M	P	C	W	O
29	27.5	0/0	60/20	0/28	0/70	0/0	70/0	100/98	50/45
A	4.4	0/0	90/90	0/0	0/0	0/0	—/100	100/100	88/100
	1.8	0/0	62/62	0/0	0/0	0/0	—/100	98/100	52/63
	0.7	0/0	37/37	0/0	0/0	0/0	—/22	65/80	40/22
	0.28	0/0	3/3	0/0	0/0	0/0	—/0	0/10	7/0
37	4.4	0/10	100/100	0/0	0/0	0/0	—/100	100/100	47/93
	1.8	0/0	98/77	0/0	0/0	0/0	—/85	100/98	45/15
	0.7	0/0	35/12	0/0	0/0	0/0	—/22	100/47	22/0
	0.28	0/	2/0	0/0	0/0	0/0	—/0	52/7	0/0
39	4.4	0/0	72/98	0/0	0/0	0/0	—/77	100/100	42/73
	1.8	0/0	62/73	0/0	0/0	0/0	—/13	98/92	0/0
	0.7	0/0	32/12	0/0	0/0	0/0	—/0	55/75	0/0
	0.28	0/0	0/0	0/0	0/0	0/0	—/0	32/0	0/0
46	11	—/5	—/87	—/0	—/32	—/25	—/13	—/100	—/100
	4.4	0/0	90/48	0/0	0/0	0/0	32/0	100/100	60/82
	1.8	0/0	60/13	0/0	0/0	0/0	3/0	100/98	45/73
	0.7	0/0	13/5	0/0	0/0	0/0	0/0	40/58	0/12
	0.28	0/—	8/—	0/—	0/—	0/—	0/—	13/—	0/—

CLAIMS

1. Compounds represented by the general formula:



5 wherein R is alkyl or 1 to 6 carbon atoms or phenyl; R¹ is haloalkyl of 1 to 6 carbon atoms, haloalkenyl of 2 to 6 carbon atoms, haloaryl of 6 to 10 carbon atoms, halobenzyl, all of which contain 1 to 3 halogen atoms, cycloalkyl of 5 to 7 carbon atoms, or benzyl substituted by 1 to 3 alkyl groups of 1 to 4 carbon atoms or haloalkyl groups of 1 to 4 carbon atoms and 1 to 9 halogen atoms; R² and R³ are independently hydrogen, alkyl of 1 to 3 carbon atoms, alkylthio of 1 to 6 carbon atoms, or alkylthioalkyl

of 2 to 8 carbon atoms; R⁴ is hydrogen, or carbalkoxy of 2 to 4 carbon atoms; and R⁵ is hydrogen, a cation, or



wherein R⁶ is alkyl of 1 to 6 carbon atoms or aryl or 6 to 10 carbon atoms.

- 5 2. Compounds as claimed in Claim 1, wherein R⁴ and R⁵ are hydrogen.
 3. Compounds as claimed in Claim 1 or 2, wherein R is alkyl of 1 to 3 carbon atoms.
 4. Compounds as claimed in Claim 1, 2 or 3, wherein R¹ is haloalkenyl of 2 to 6 carbon atoms and
 1 to 3 halogen atoms, or halobenzyl of 1 to 3 halogen atoms.
 5. Compounds as claimed in Claim 1, 2, 3 or 4, wherein R² and R³ are alkyl of 1 to 3 carbon atoms.
 10 6. 2-[1-(3'-Chloroallyloxyamino)-butylidene]-5,5-dimethylcyclohexane-1,3-dione.
 7. 2-[1-(3'-Chloroallyloxyamino)-propylidene]-5,5-dimethylcyclohexane-1,3-dione.
 8. A process for preparing a compound as claimed in Claim 1, wherein R⁵ is hydrogen,
 substantially as described in either of the foregoing Examples.
 9. A herbicidal composition comprising a biologically inert carrier and a herbicidally effective
 15 amount of a compound as claimed in any one of Claims 1 to 7.
 10. A method of killing vegetation which comprises applying to said vegetation or its growth
 environment a herbicidally effective amount of a compound as claimed in any one of Claims 1 to 7.
 11. A method according to Claim 10, wherein the vegetation is crabgrass, watergrass or wild oats.

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